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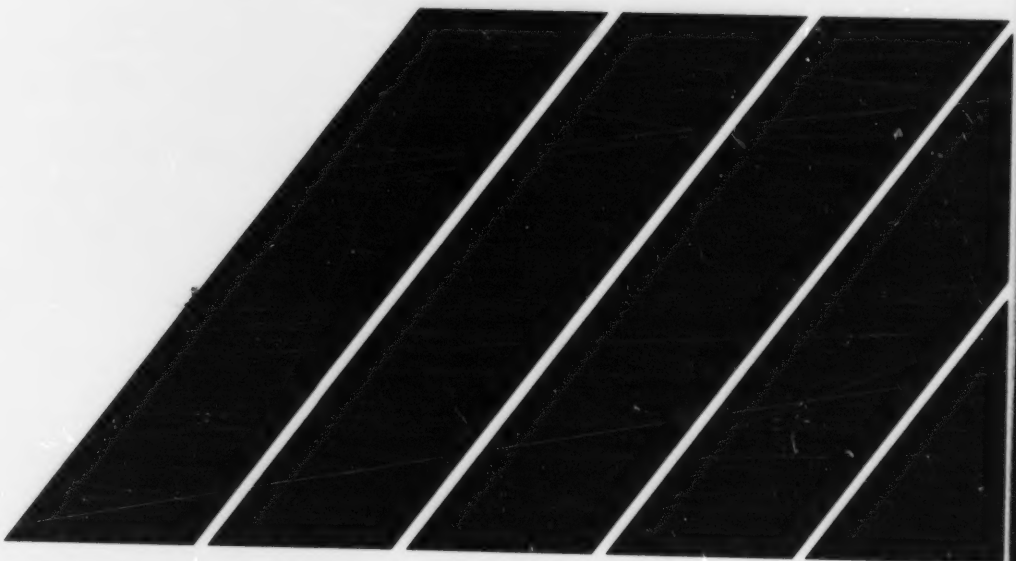
Direction de la technologie de l'efficacité énergétique et des énergies de remplacement

PRELIMINARY STUDY ON VACUUM PYROLYSIS OF LIGNIN BY-PRODUCT MATERIALS DERIVED FROM STEAM-EXPLODED WOOD, PHASE I: LABORATORY STUDY



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PRELIMINARY STUDY ON VACUUM PYROLYSIS OF LIGNIN BY-PRODUCT MATERIALS DERIVED FROM STEAM-EXPLODED WOOD, PHASE I: LABORATORY STUDY

PREPARED FOR:

Efficiency and Alternative Energy Technology Branch
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PREFACE

This work was performed by Carbovac Research Inc. under contract to the Department of Supply and Services (DSS Contract No. 048SZ.23283-8-6173) over a 12-month period ending November 30, 1989.

The research is intended to provide preliminary information for the conversion of lignin by-product materials derived from steam-exploded wood by vacuum pyrolysis. The experimental data are useful as a basis for technical evaluation of the processing concept.

The work fits within the general objectives of the Efficiency and Alternative Energy Technology Branch to promote a better use of biomass as a source of fuels and chemicals. The vacuum pyrolysis approach is one of the thermoconversion routes currently supported by the Branch.

The intended audience for this report includes other contractors in this field, representatives of the biomass industry in Canada and elsewhere, equipment manufacturers, and the scientific community in general.

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EXECUTIVE SUMMARY

The main objective of this study was to investigate the potential of vacuum pyrolysis as a means of recycling and upgrading lignin by-product materials from steam-exploded wood. The source material was provided by Iogen Corporation in Ottawa. The UM grade lignin was produced from aspen wood.

The pyrolysis experiments were performed in a laboratory scale, batch reactor unit, with 100 g of feedstock material. The maximum pressure reached during a run was 2 kPa absolute. Highest yield of oil from preliminary, non-optimized experiments was obtained at 465°C. Pyrolysis oil yield reached 43% by wt. based on the anhydrous and ash-free lignin feedstock. Together, the charcoal and oil yields represented approximately 80% of the initial feedstock biomass. The gross calorific value of these two products is high at 22,500 kJ/kg (oil) and 31,500 kJ/kg (charcoal).

A detailed chemical analysis of this oil was made. First the oil (including all liquids: water, water-soluble, organics and water-insoluble tar) was fractionated into different fractions using a preparative Liquid Chromatography (LC) method. A 0.5 g of oil was fractionated into eight fraction on 15 g of activated and pre-washed silica gel using various solvents with an increasing polarity. Quantitative recovery (>95%) of the oil was obtained after fractionation.

The first seven fractions (F1 to F7) which represented 45% by weight of the water and acid-free oil were then analysed by GC-MS method. These tests revealed that F1 and F2 were mainly saturated (alkanes) and unsaturated (aromatics) hydrocarbons, respectively. F3 to F7 fractions were much interesting, since all their peaks were well separated, resolved and characterized without difficulty. F3-F7 were mainly phenolic, aldehydic, ketonic and alcoholic compounds with increasing polarity from the low polar methoxy benzene to the high polar diphenolic and aldehydic compounds.

Some of the major compounds found in the lignin pyrolysis oil are the following: 3, 4, 5-Trimethyl-2-cyclopentene-1-one (0.6%); Phenol (0.8%); 2,6-Dimethoxy-4-(2-propenyl) phenol (2.3%); 3-Methoxy-1,2-benzenediol (1.2%); catechol (1.2%) and syringaldehyde (0.4%). Many other

compounds which were detected in F3-F7 were not quantitated since the standards were not available. Also, due to their high polarity and presumably their high molecular weights, the compounds present in F8 could not be analysed by GC. F8 which accounted for 55% of the oil possibly contained several high value chemicals as well.

Most of the chemicals identified (and partially quantified) in F3-F7 are phenolic types which have various applications, for example, pharmaceutical. Alternatively, those chemicals can be used in mixture for the manufacture of phenol-formaldehyde adhesives and prepolymers. The latter application, in particular, has been suggested as quite interesting on a commercial basis. An immediate use would also be to blend the charcoal and oil together with the pyrolytic water and used it as a blend fuel for steam generation or electricity production.

RESUME

L'objectif principal de cette étude consistait à évaluer le potentiel du procédé de la pyrolyse sous vide comme moyen de recycler et utiliser de façon profitable les sous-produits ligneux dérivés d'un processus de fractionnement à la vapeur du bois. Le matériau testé provient de l'opération de la Iogen Corporation et la lignine, grade UM, a été obtenue du bois de peuplier faux-tremble.

Les expériences de pyrolyse ont été effectuées à l'échelle du laboratoire dans un réacteur en vrac pouvant recevoir 100 g de biomasse à la fois. Ce système opérait à une pression totale de 2 kPa au maximum durant un essai. Les rendements en huiles les plus élevés, basés sur des essais préliminaires et non optimisés, ont été obtenus à la température de 465°C. A cette température, les rendements en huiles sur la base du matériau sec de départ et sans cendres était voisin de 43% massique. Au total, l'ensemble des huiles de pyrolyse ainsi que le charbon résiduel représentaient environ 80% de la masse initiale alimentée. Le pouvoir calorifique supérieur de ces deux produits de la pyrolyse est assez élevé, soit 22 500 kJ/kg pour les huiles et 31 500 kJ/kg pour le charbon.

On a tenté une analyse chimique plus détaillée de ces huiles. On a d'abord effectué le fractionnement de l'ensemble des condensats liquides (incluant l'eau, les matières organiques solubles dans l'eau et les goudrons insolubles) au moyen d'une de chromatographie liquide préparative (CL). On a obtenu de cette façon huit fractions différentes au moyen d'une colonne chromatographique d'échelle analytique et garnie de 15 g de gel de silice activé et prélavé. On versait à la tête de cette colonne 0.5 g des huiles de pyrolyse puis on éluait la colonne au moyen de différents solvants de polarité croissante. Une bonne récupération des produits (>95%) a été constatée au terme de ces essais.

Les sept premières fractions obtenues (F1 à F7) représentaient approximativement 45% en poids des huiles sur une base anhydre et sans acides gras. On a procédé à une analyse en mode CG-SM (chromatographe en phase gazeuse couplée à un spectromètre de masse) de toutes ces fractions. Ces essais ont révélé que les fractions F1 et F2 étaient majoritairement constituées d'hydrocarbures de type alcanes et aromatiques, respectivement. Les fractions F3 à F7 se sont

révélées particulièrement intéressantes pisqu'il a été possible d'atteindre un dégré élevé de séparation et de résolution des pics. F3-F7 regroupent essentiellement des composés phénoliques, aldéhydiques, cétoniques et alcooliques dont la polarité allait croissante depuis les composés de faible polarité comme le méthoxybenzène jusqu'aux composés plus polaires comme les substances de caractère diphénolique et aldéhydique.

On a identifé entre autres dans ces huiles de pyrolyse les composés suivants:

- 3,4,5-triméthyl-2-cyclopentène-1-one (0,6%)
- phénol (0,8%)
- 2,6-diméthoxy-4(2-propenyle) phénol (2,3%)
- 3-méthoxy-1, 2-benzènediol (1,2%)
- catéchol (1,2%)
- syringaldéhyde (0,4%)

On a aussi détecté plusieurs autres substances dans les fractions F3 à F7 qu'il n'a pas été possible de quantifier parce que les standards n'étaient pas tous disponibles. Egalement, il n'a pas été possible d'analyser les composés présents dans la fraction F8, à cause de leur polarité élevée et de leur poids moléculaire vraisemblablement assez élevé. La fraction F8 qui représentait 55% de l'huile renferme possiblement aussi plusieurs composés chimiques de haute valeur commerciale.

Un grand nombre des produits chimiques qui ont été identifiés (et partiellement quantifiés) dans F3-F7 sont des composés phénoliques dont les usages pharmaceutiques multiples à titre d'exemple, sont bien établis. Alternativement, on peut utiliser ces produits chimiques sous forme d'un mélange pour la fabrication de matériaux adhésifs et de prépolymères à base de phénol-formaldéhyde. On a d'ailleurs suggéré ailleurs qu'une telle application représentait une opportunité commerciale attrayante. Un autre usage plus immédiat consisterait aussi à mélanger le charbon ainsi que l'huile et l'eau pyrolytique afin de former un nouveau combustible qui pourrait être utilisé pour la production de vapeur ou d'électricité.

INTRODUCTION

Ethanol produced from biomass is a plausible alternative to gasoline. The technology is available, but the capital investment required, the operating costs including the feedstock cost, are high. Economists predict that ethanol will compete with petroleum only when prices will significantly exceed 30$/bbl.

Fuel ethanol's primary advantage is environmental. It is a much cleaner-burning fuel than gasoline. When derived from sustainable biomass, it is the only liquid transportation fuel that does not contribute to the greenhouse effect. A successful demonstration of the economic production of liquid fuels and chemicals from lignin would significantly enhance the prospects for commercial production of fuels including ethanol from biomass. However, the key for commercialization is efficient separation, economical recovery, and quality control.

This research is intended to provide preliminary information for the conversion of lignin by-product materials derived from steam-exploded wood by vacuum pyrolysis. The main products of lignin pyrolysis are charcoal and pyrolysis oil. Lignin-derived charcoal can be used, for example, to produce activated charcoal, coke, semi-coke and carbon electrodes. The pyrolysis oil and charcoal can be used as fuels. Alternatively, the pyrolysis oil which is rich in phenolic compounds can be used for the preparation of adhesives and phenolic resins. High-value chemicals can also be separated and purified which could be used in the pharmaceutical, food and perfume industries. These chemical by-products can significantly improve the feasibility of the wood-exploded process. The experimental data provides a useful basis for the technical evaluation of the processing concept.

OBJECTIVES

The main objective of this study was to investigate the potential of vacuum pyrolysis as a means of upgrading the lignin by-products derived from steam-exploded wood.

Two specific objectives were the following:

- To test the validity of using the vacuum pyrolysis concept by producing liquid fuels and charcoal from lignin.

- To undertake a preliminary study of the influence of the reactor operating conditions over the liquid, solid and gas yields, as well as the composition of oils produced by vacuum pyrolysis of lignin from steam-exploded wood.

EXPERIMENTS

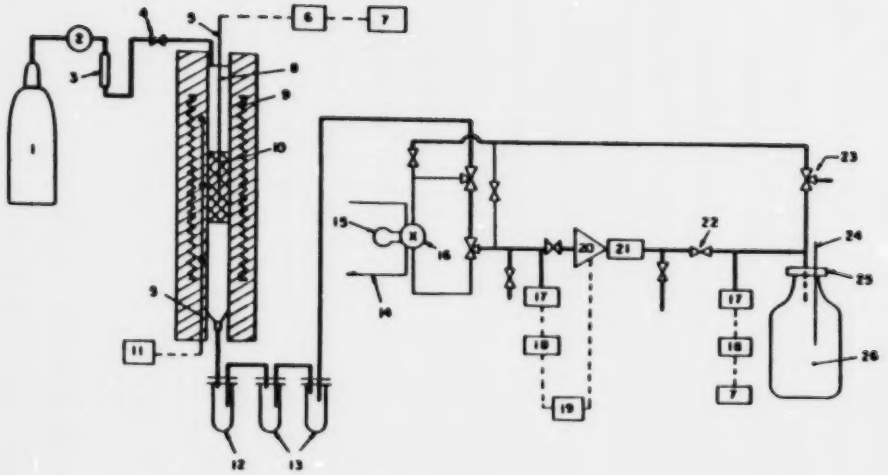
Pyrolysis Experiments

The laboratory scale batch reactor unit used in this work is shown in Figure 1. The stainless steel reactor was externally heated by means of electrical resistance heaters. The temperature, pressure and heating rate of the system were monitored by a microcomputer system.

The reactor was fed batchwise with approximately 100 g of feedstock. The reactor was initially heated to 100°C and then increased up to 465°C at a rate of 3°C min^{-1}. The maximum pressure during a run was lower than 2 kPa (abs). The vapour products were condensed in three condensers connected in series which were maintained at 0°C, - 80°C and -80°C, respectively. The first trap was cooled by water and ice. The two others were cooled with dry ice and acetone. The non-condensable gas was pumped into a metallic gas container by a mechanical vacuum pump. At the end of a run, the liquid and solid products were weighed, the gas was analysed and the mass balance was calculated. The condensates were an aqueous phase (water soluble organics and water) and an organic liquid phase (water insoluble organics) which could be separated by decantation. Both phases were recombined for the analyses.

Standard Methods for Lignin Feedstock and Solid Residue Characterization

A 1 kg. sample of "UM grade" lignin was provided by Iogen Corporation. This lignin is a by-product of an enzyme hydrolysis process for the production of ethanol from biomass. It was prepared by a steam explosion treatment of aspen wood according to the conditions of European Patent No. 0044658 (1983). The exploded aspen wood was then treated with a cellulase enzyme to hydrolyze the carbohydrate fraction of the wood to soluble sugars. The hydrolysis proceeded to approximately 85% of completion. The residual material (UM Lignin), which contained approximately 25% cellulose and essentially no hemicellulose, was then washed with water to remove soluble sugars and dried.



LEGEND:

1. Nitrogen cylinder
2. Pressure gauge
3. Rotameter
4. Micrometric valve
5. Thermocouple
6. Thermocouple meter
7. Recorder
8. Retort
9. Three zone electric furnace
10. Sample
11. Temperature programmer
12. Cooling trap (ice and water)
13. Cooling traps (dry ice and acetone)
14. Carrier gas to chromatograph
15. Sampling loop
16. Gas sampling valve
17. Electronic manometer head
18. Digital readout
19. Pressure controller
20. Automatic vacuum exhaust valve
21. Vacuum pump
22. Two-way manual valve
23. Three-way manual valve
24. Thermometer
25. Vacuum seal
26. Gas collecting bottle

Figure 1 Schematic of the Vacuum Pyrolysis Bench Scale System

Characterization tests were performed on the as-received logen lignin and the charcoal samples according to ASTM methods. The names and identification numbers of the methods used are listed in Table 1.

Table 1 - List of Standard Methods Used to Characterize the Feedstock and Solid Residues

Test	Lignin	Lignin-Charcoal
Moisture	D2016	D1762*
Ash	D1102*	D1762*
Volatile Matter	E872*	D1762*
Fixed Carbon	E872*	D1762*
Gross Calorifc Value	E711	D2015
Elemental Analysis	Carlo Erba model 1106 apparatus (0 by diff.)	
Sulfur	Leco model SC-32 apparatus	

* Using the Leco MAC-400 determinator

Gaseous Product Analysis

Analysis of the gas was made by direct injection of the total gas into the gas chromatograph after termination of the pyrolysis reactions. The gas chromatograph was equipped with two stainless steel columns (183 cm each) in series, packed with Porapak-Q (80-100 mesh), Molecular Sieve 5 Å (60-80 mesh), and TC detector. The GC oven temperature was programmed as below. The oven was maintained at 50°C for four minutes then programmed to 240°C at a rate of 8°C min^{-1}.

Pyrolysis Oil Analysis

Gas Chromatographic (GC) and Gas Chromatographic-Mass Spectrometric (GC/MS) analyses of the lignin-derived pyrolysis oils were made. Because of its complex composition, lignin pyrolysis oil was fractionated using a Liquid Chromatography (LC) method prior to GC/MS

analyses. The method of fractionation was adapted, with slight modification, from recently published (1) wood pyrolysis oil methodology. In this method 0.5 g of the oil is transferred to a glass column already packed with 15 g of activated and pre-washed silica gel (60 - 120 mesh). The column was then eluted with 150 ml of various solvents with increasing polarity. Nature of the solvents used and the volume and weight of the collected fractions are shown in Table 2. Quantitative recovery (≥ 95%) of the oil was obtained after fractionation. Weight percentages of the fractions are on a water-and acid-free oil basis. Since water was strongly and irreversibly adsorbed on the silica-gel surface, the total water content in the oil was measured by Karl-Fisher technique before fractionation (2).

Gas-chromatographic analysis were made with a Varian 6000 gas chromatograph with split injection mode on a 50 m x 0.2 mm i.d., HP5, capillary column. Oven initial temperature was held at 50°C for 2 min then heated up to 290°C at 5°C min^{-1}. Injection and FID temperatures were 290°C and 300°C, respectively. A waters 840 data and chromatography control station with Digital Professional 350 computer and LA50 recorder were used as the data processor. GC-MS analyses were performed by BC Research on a bench type Quadrupole Hewlett-Packard MSD attached to a 5890 GC.

Table 2 Yields of Various Fractions Obtained by Liquid Chromatographic Separation of Lignin Pyrolysis Oil

Fraction #	Solvent	Yield* (wt%)
1	100% Petroleum Ether	2.8
2	20% Dichloromethane in Petroleum Ether	0.6
3	40% Dichloromethane in Petroleum Ether	5.5
4	60% Dichloromethane in Petroleum Ether	3.4
5	80% Dichloromethane in Petroleum Ether	7.5
6	100% Dichloromethane	4.8
7	100% Diethyl Ether	20.4
8	10% Methanol in Ethylacetate	55.0

* Based on anhydrous and acid-free pyrolysis oil

RESULTS AND DISCUSSION

Lignin Characterization

The following chemical properties of the lignin powder were determined in our laboratory:

Moisture:	1.2%
Ash:	1.2%
Volatile Matter:	67.9%
Fixed Carbon:	30.9%
Gross Calorific Value:	25.2 MJ/kg
Elemental analysis:	
C:	58.17%
H:	5.98%
N:	0.98%
O:	34.8%
S:	0.07%

According to the manufacturer, the Na, Ca and Si content was 0.34%, 0.28% and 0.55%, respectively. The UM lignin had a methoxy content of 13.9%.

This lignin sample was a by-product from the steam-explorin process of Iogen Corp. The product is characterized by a very fine granulometry as follows:

Particle diameter (μm)	Wt. %
d > 1000	0.09
500 < d < 1000	0.64
250 < d < 500	71.80
25 < d < 250	6.37
45 < d < 125	16.55
d < 45	4.55
	100.00

For the pyrolysis tests, the lignin powder was densified to small cylinders with 13 mm in diameter and 12 mm thick and with a bulk density of 0.6 g/cm^3. Otherwise, the fine particles were drawn out of the chamber by sucking the gas with the mechanical pump.

Table 3. Yields and Mass Balance on Vacuum Pyrolysis of UM Lignin

	Exp. # A049	Exp. # A050
Max. temp. (°C)	465	400
Abs. pressure (kPa)	2	1.3
Heating rate (°C/min)	15	12
Mass balance closure (%)	98.89	99.49
Yields (wt. %, moisture and ash-free lignin basis)		
Charcoal	38.04	44.44
Oil*	42.69	34.51
Gas	10.01	8.52
Pyrolytic Water**	9.26	11.20

* Water soluble and insoluble organics
** Determined by the Karl Fischer method

Yields and Mass Balance

The pyrolysis of lignin yielded four different phase products: a solid phase (charcoal), an organic phase (oil), an aqueous phase (water + water soluble organics) and a noncondensable gas phase. The product yields and mass balance for the two pyrolysis experiments conducted with the UM lignin are listed in Table 3. The main pyrolysis product was oil with a yield of 42.69% at 465°C . The gross calorific value of this type of oil is generally in the range of 22,500 kJ/kg (anhydrous basis). Together, the charcoal and oil yields represented approximately 80% of the anhydrous and ash-free feedstock material.

The small material loss experienced during the runs was attributed to the gas phase. Overall, the mass balance closure was found to be quite satisfactory.

The gas analysis results are shown in Table 4 on a volume % basis and on a weight % basis in Table 5. Carbon dioxide, carbon monxide and methane were the most abundant gases.

The proximate and ultimate analyses of the lignin-derived charcoal product are given in Table 6. The charcoal calorific value is substantially higher than that of the feedstock which is an asset if the pyrolysis product is to be burned for energy generation.

Two pyrolysis runs were carried out during this study. The first objective was to investigate the influence of the decomposition temperature on the oil production. The first run was designated as logen A049 and was conducted at 465°C. The second run was designated as logen A050 and was conducted at 400°C. The results showed a significant oil yield enhancement as the pyrolysis temperature was increased from 400 to 465°C.

Table 4 - Gas Phase Composition (vol. %)

	logen A049	logen A050
CH_4	18.55	16.50
CO	33.37	31.85
CO_2	44.73	48.70
C_2H_4	0.75	0.52
C_2H_6	0.93	0.57
Others	1.67	1.86
Gross calorific value, MJ/kj	9.2	8.2
Mean molecular weight, g/mole	33.5	34.5

Table 5 - Yields of Individual Gaseous Components
(wt. %, water and ash-free wood basis)

	Iogen A049	Iogen A050
CH_4	0.88	0.65
CO	2.79	2.19
CO_2	5.87	5.25
C_2H_4	0.06	0.03
C_2H_6	0.08	0.04
Others	0.81	0.29

Table 6 - Chemical Analysis of the Lignin-Derived Charcoal

	Exp. # A049	Exp. # A050
Moisture (%)	1.22	2.47
Ash (%)	3.05	2.39
Volatile Matter (%)	21.96	26.33
Fixed C (%)	74.99	71.28
C (%)	77.70	74.44
H (%)	3.46	3.53
N (%)	1.08	1.11
O (%)	17.73	20.89
S (%)	0.03	0.03
Gross Calorific Value (MJ/kg)	31.8	31.2

Chemical Analysis of the Pyrolysis Oils

Lignin is one of the principal wood components which accounts for about 20% of hard woods on an anhydrous basis. It has a complex polymeric structure with various functional groups attached to the aromatic rings (see Figure 2). Raw lignin has few industrial applications. It is mainly a by-product of the wood-pulping industries. Due to its low potential application, the lignin by-product materials are generally piled or uselessly discarded.

Vacuum pyrolysis of biomass produces high yield of oil which contains various valuable, rare and commodity chemicals, depending on the source materials. Economical recovery of valuable chemicals like food aromas and pharmaceutical compounds could really increase the profitability of the process. We found that the lignin pyrolysis oil with its phenolic nature will have a potential application if it is fractionated either into pure compounds or classes of compounds. This study is a preliminary investigation on the potential application of lignin oil obtained by vacuum pyrolysis. However, efficient separation and purification of these chemicals is a critical process and requires further investigation.

Figure 3a represents a complex chromatogram of the total lignin pyrolysis oil (Run # A049). Chromatograms of F1 to F7are illustrated in Figures 3b to 3h. Due to their high polarity and presumably their high molecular weights, the compounds present in Fraction 8 could not be analysed by GC. F1 and F2 are mainly saturated and aromatic hydrocarbon mixtures, respectively. Fractions 3 to 7 are of greatest potential interest, since all the peaks are sufficiently separated and resolved and could be characterized almost without ambiguity.

The fractionation was successful with only partial coelution of compounds over two successive fractions. F3 to F7 were mainly concentrated with phenolic, aldehydic, ketonic and alcoholic compounds with increasing polarity from low polar methoxy benzene (e.g., F3) to high polar diphenolic and aldehydic compounds (e.g., F7). A detailed GC/MS analysis of F3 to F7 is presented in Table 7.

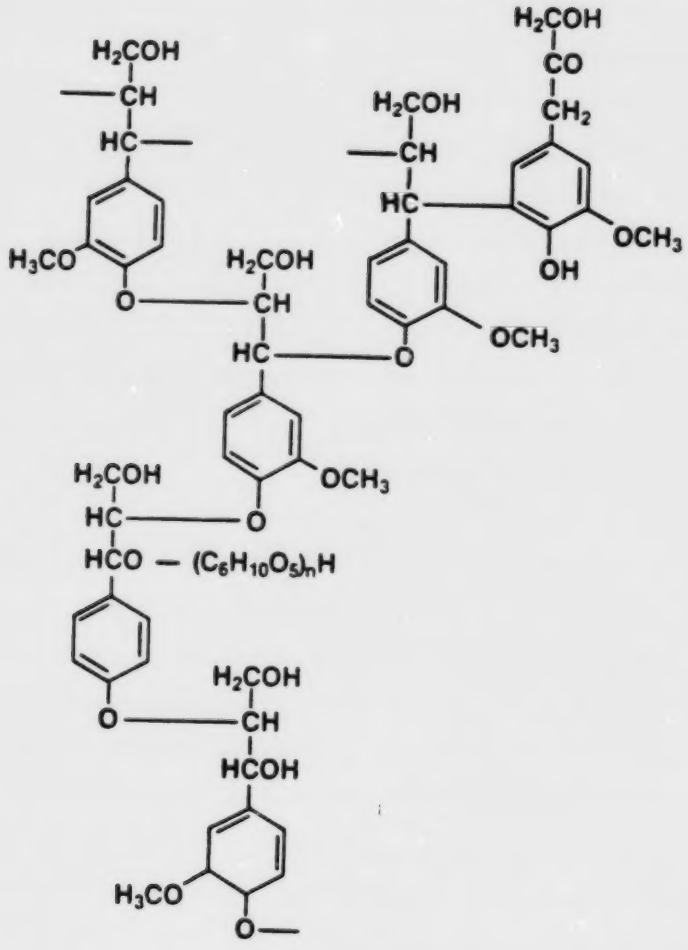


Figure 2 Typical Lignin Structure Representation

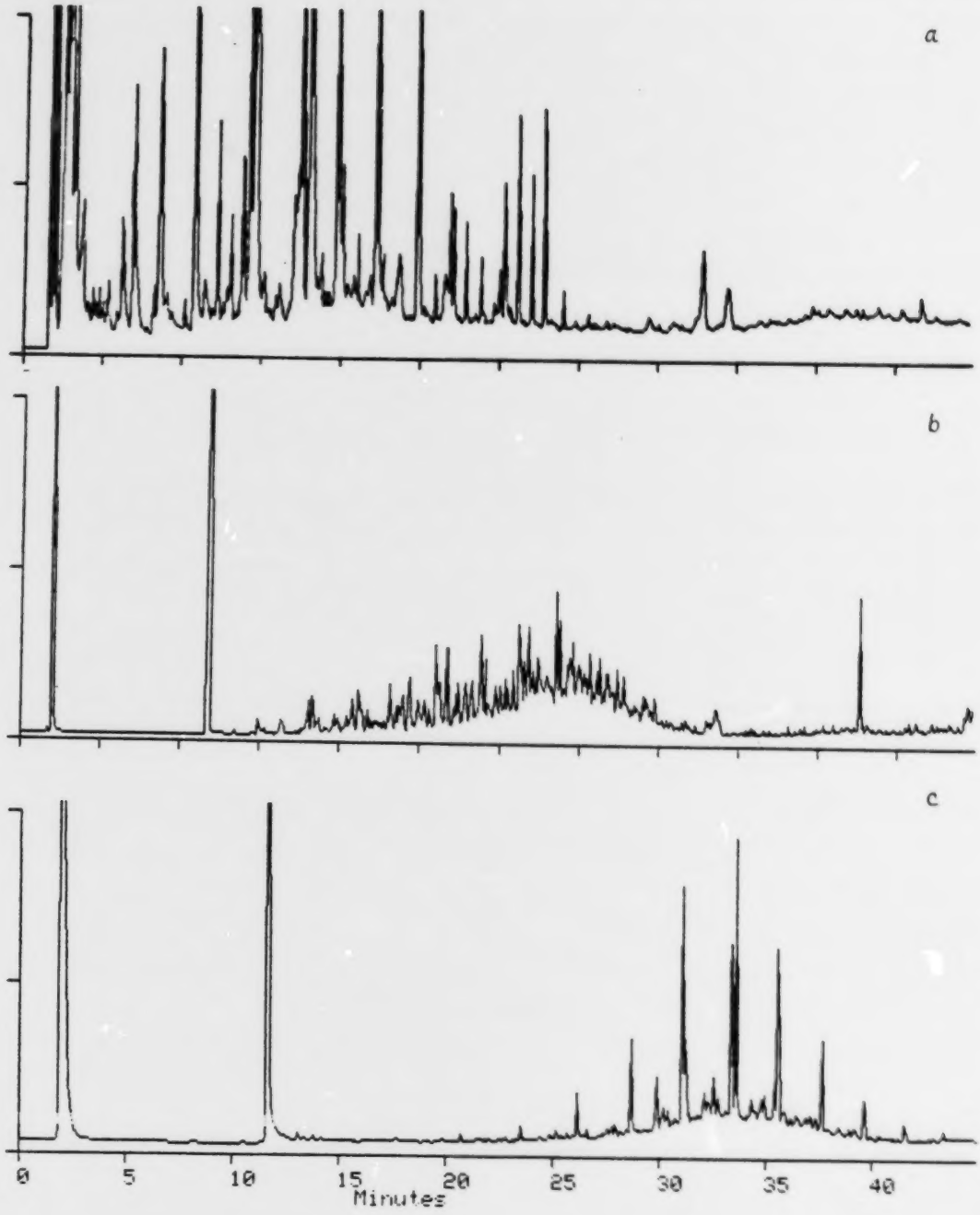


Figure 3 Gas Chromatograms of Lignin Pyrolysis Oils: (a) total oil; (b-h) F1 to F7

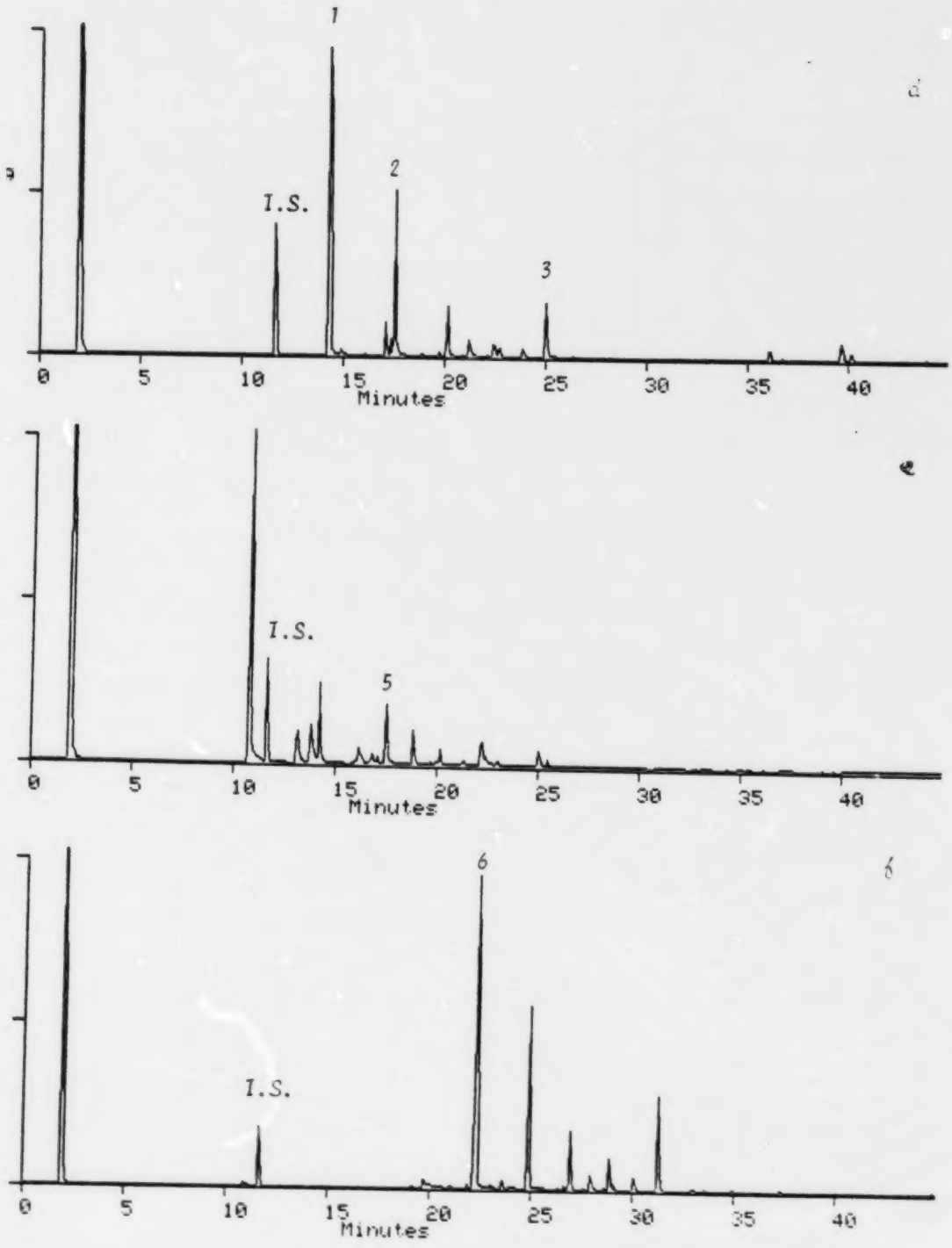


Figure 3 Continued

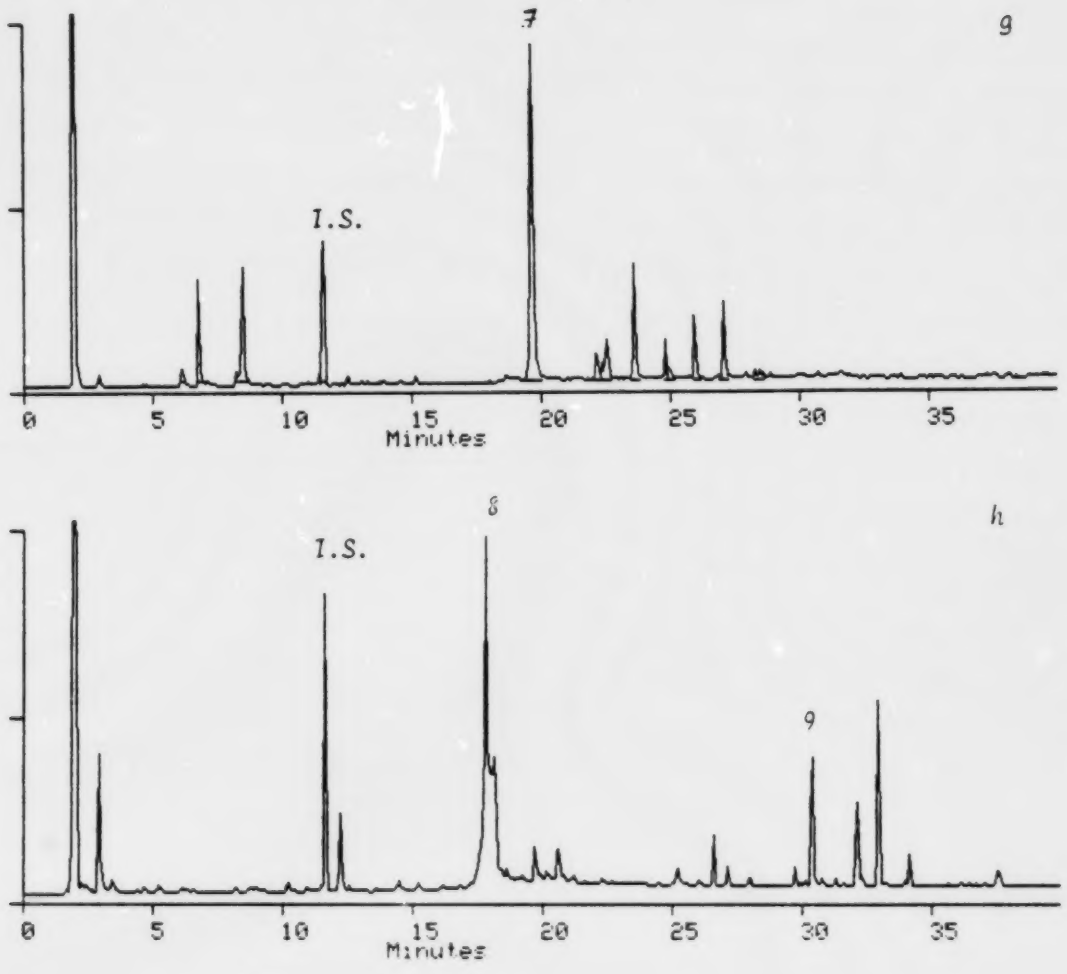


Figure 3 Continued

Precise quantification of all the organic compounds listed in Table 7 would require the corresponding standards. We had only a few standards available during this investigation, therefore we were unable to quantify some of the highly concentrated chemicals identified in this oil.

The method of fractionation is particulary interesting since it allowed to separate oil into several simple subfractions for unambiguaus GC/MS analyses. It also enabled us to separate a fraction, which could not be analysed by GC or GC/MS due to its low volatility and/or high polarity or high reactivity. The preparative separation and purification of compounds with high commercial value requires further work. Since many of these oxygenated compounds, mainly of phenolic nature, are high value compounds and are not commercially available, their separation and purification, even in low concentration, could be very valuable and will certainly lead to the discovery of many more compounds with potential applications. In addition, individual fractions (e.g., Fractions 3 or 4) can possibly be utilized in bulk for fabrication of phenolic resins (3).

Besides Fractions 3 to 7 which contain valuable chemicals of phenolic nature, Fraction 8 which accounts for 55% of the oil, may contains several high value chemicals that could not be identified during this present study.

Table 7 - Major Compounds Found in Various Fraction of the Lignin Pyrolysis Condensates

Fraction #	GC Peak #	Compound Identied by GC-MS	Yield*
3	1	3,4,5-Trimethyl-2-cyclopentene-1-one	0.6
	2	2-Methoxy-4-methylphenol (creosol)	0.2
		4-Ethyl-2-methoxyphenol	
	3	Isoeugenol	0.1
		Methyl 16-methyl-heptadecanoate	
4	4	Phenol	0.8
		2-Methylphenol (o-cresol)	
		4-Methylphenol (p-cresol)	
		2,3,4-Trimethyl-2-cyclopentene-1-one	
		3,4- or 2,4-Dimethylphenol	
		3,5 Dimethylphenol	
	5	2-Methoxy-4-methylphenol	0.2
		4-Ethyl-2-methoxyphenol	
		2,6-Dimethoxyphenol (syringol)	
5		3-Methoxy-1,2-benzenediol	
		2,6-Dimethoxyphenol (syringol)	
	6	2,6-Dimethoxy-4-(2-propenyl)phenol	2.3
6		2-Methyl-2-butenal	1.2
	7	3-Methoxy-1,2-benzenediol	
		or 2-Methoxy-1,4-benzenediol)	
		3-Methyl-1,2-benzenediol	
		3,4-Dimethoxyphenol	
		1-(4-Hydroxy-3-methoxyphenyl)ethanone	
		1-(4-Hydroxy-3-methoxyphenyl)-	
		2-propanone	
7		3-Methyl-2-cyclopentene-1-one	
		2-Hydroxy-3-methyl-2-cyclopentene	
		-1-one	
	8	1,3-Benzenediol (catechol)	1.2
		3-Methoxy-1,2-benzenediol	
		3-Methyl-1,2-benzenediol	
		4-Ethyl-1,3-benzenediol	
		2,6-Di-t-butyl-4-methylphenol	
	9	Syringaldehyde	0.4
		1-(4-Hydroxy-3,5-dimethoxyphenyl) ethanone	
		1-(2,4,6-Trihydroxy-3-methylphenyl)	
		-1-butanone	

* Wt.% of Total Lignin Pyrolysis Condensates
(Condensates include: water, water soluble organics and water insoluble organics)

Application and Market Value of Lignin Pyrolysis Oil

We mentioned that lignin pyrolysis oils could be utilized as a source of specialty chemicals after separation and fractionation. It has long been known that phenolic compounds have pharmaceutical as well as industrial applications. Table 8 lists the applications and market value of typical lignin-base compounds. Of course their abundance in the pyrolysis oils strongly depends on the pyrolysis conditions and the source materials.

The approach followed in this investigation was to fractionate the pyrolysis oil into various classes based on their polarity on an analytical scale between 0.5 to 1 g. The feasibility of scaling up the wood pyrolysis concept to a pilot scale has been investigated (14). This study showed that the process feasibility will be significantly improved if the chemical by-products present in the condensates are recovered. A preliminary feasibility study of scaling up the liquid chromatography fractionation method describe in this report indicated that more research and develop is needed to decrease the volumes of solvents used during the extration steps (5). Work is continuing along this line in our laboratories. Unlike the whole biomass pyrolysis oil, lignin pyrolysis oil is mainly phenolic in nature and therefore no further purification is needed if a group of compounds is to be utilized. Any or all of the Fractions 2 to 7, for example, could be used in bulk for the manufacture of phenol-formaldehyde adhesives and prepolymers (3) or further purified to isolate single compounds. F2 to F7 accounted for approximately 42% of the total oil. Recently, Diebold and Power (3) conducted a preliminary feasibility study of a fast wood pyrolysis plant, followed by a solvent extraction step to produce mixtures of phenolic and neutral compounds useful for phenol-formaldehyde resin formulations. Their study showed prices of about $0.17 U.S. per pound of phenol/neutral fraction after wood pyrolysis and solvent extraction compared to the present market value of phenol of $0.36-0.41 U.S. per pound. Certainly lignin vacuum pyrolysis oil would be fairly promissing if the fractionation is scaled-up since there is no further purification and interference from the non-phenolics for the formulation of adhesives or resins.

Table 8 - Application and Market Value of Typical Lignin-Base Compounds which are Found in Pyrolysis Oils

Compound	Typical usages	Price (U.S. $/kg in 1986)
Phenol	Disinfectant/organic synthesis	0.79-0.93
Camphor	Plastic/medicines	3.96-7.70
Cresol	Disinfectant/solvent/photography/ phenolic resins	1.90-3.80
Eugenol	Analgesics/insecticide	8.59-12.89
Guaiacol	Pharmaceutical industry	5.95
Creosol	Pharmaceutical industry	3.3-3.4
Isoeugenol	Chemical synthesis	11.69-12.33
Catechol	Photography/dyeing agent/antiseptic	3.71-7.93
Thymol	Antifungal/antiseptic	7.50-12.30

CONCLUSIONS

Some of the major compounds found in the lignin pyrolysis oil are the followings: 3, 4, 5-Trimethyl-2-cyclopentene-1-one (0.6%); Phenol (0.8%); 2,6-Dimethoxy-4-(2-propenyl) phenol (2.3%); 3-Methoxy-1,2-benzenediol (1.2%); catechol (1.2%); and syringaldehyde (0.4%). Many other compounds which were detected in F3-F7 could not be quantitated since the standards were not available. Also, due to their high polarity and presumably their high molecular weights, the compounds present in F8 could not be analysed by GC. F8, which accounted for 55% of the oil possibly contained several high value chemicals as well.

A large number of the chemicals which were found in F3-F7 were phenolics which have pharmaceutical applications, for example. Alternatively, those chemicals can be used in a mixture for the manufacturing of phenol-formaldehyde adhesives and prepolymers. This last application in particular has been found to be quite attractive on a commercial basis elsewhere (3).

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